Evidence for Stable High Temperature Ferromagnetism in Fluorine Treated C_{60}

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Abstract

It is shown by magnetic field dependent ac susceptibility, magnetic force microscopy, and ferromagnetic resonance that exposure of C_{60} to fluorine at 160 ^{0}C produces a stable ferromagnetic material with a Curie temperature well above room temperature. The exposure to fluorine is accomplished by decomposing a fluorine rich polymer, trifluorochloroethylene, $[F_2C\text{-}CFCl]_n$ which has C_{60} imbedded in it. Based on previous experimental observations and molecular orbital calculations, it is suggested that the ferromagnetism is arising from crystals of C_{60}-F.

Key words: C_{60}-dimer, fluorine, ferromagnetism, AC susceptibility, ferromagnetic resonance, magnetic force microscopy

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14. ABSTRACT
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INTRODUCTION

There has been much interest in the material science community in synthesizing molecular based ferromagnetic materials because of the potential to chemically engineer their properties and the possible ease of production. The C_{60} molecule has played an important role in this possibility because of a number of reports of ferromagnetism in it. In 1991 a complex of C_{60} and the strong electron donor molecule $C_2N_4(CH_3)_8$ (TDAE) was found to be ferromagnetic at 16.1 K.[1] Subsequently ferromagnetism having a Curie temperature of 500 K was reported in a two dimensional polymeric form of C_{60} produced by high pressure (6 GPa) and high temperature in the vicinity of 1000 K.[2,3,4] It is known that C_{60} when subjected to UV light forms oligomers most of which are dimers. [5] It has been reported that when the photolysis is done in the presence of oxygen the material is ferromagnetic well above room temperature.[6,7] There are number of reports of ferromagnetism in halogenated C_{60}. C_{60} subjected to a heat treatment in the presence of iodine was shown to be ferromagnetic having a Curie temperature of 60 K [8,9] Doping with a mix of iodine and bromine produced a material which was ferromagnetic below 30 K.[10,11]

In this work it is shown by magnetic field dependent AC susceptibility, magnetic force microscopy and ferromagnetic resonance that C_{60} treated with fluorine is ferromagnetic well above room temperature. The C_{60} was exposed to fluorine by embedding it in a fluorine rich polymer, poly trifluorochloroethylene, $[F_2C\text{-}CFCl]_n$,(PTFCE) and decomposing the polymer- C_{60} mix at high temperature to produce fluorine.

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EXPERIMENTAL

The paramagnetic and ferromagnetic resonance measurements were made using a Varian E-9 spectrometer operating at 9.2 GHz with 100 KHz modulation. The temperature of the sample was controlled by flowing heated or cold nitrogen gas through a doubled-walled quartz tube, which is part of an ADP Heli-Tran system. This system is inserted through the center of the microwave cavity. The magnetization was obtained by measuring the magnetic field dependence of the AC susceptibility at 350 kHz using a method similar to that described by Clover and Wolf [12]. The system consists of an HP 204C LC oscillator modified to have an external coil. The sample is contained in the coil, which is in a cryogenic dewar between the poles of a magnet. The change in the frequency of the oscillator, which is proportional to the change in susceptibility, is measured as a function of dc magnetic field strength using a HP 5314 frequency counter. The relative susceptibility as a function of dc magnetic field is measured by taking the difference in frequency between zero field and a given applied field. This method of measuring the susceptibility is quite sensitive but not widely used. Magnetic force microscope images were obtained using a Veeco Nano scope IV equipped with a magnetic tip. Raman measurements were made using a J.Y. Horiba confocal micro-Raman system employing a 25 mW He-Ne laser having a wavelength of 632.8 nm and focused to a spot of a 15 micron radius.

Crystalline C_{60} ,having 99.99% purity, was obtained from the Aldrich chemical company. Polytrifluorochloroethylene (PTFCE) was obtained from the Halocarbon Products Corporation. In this paper we will report clear evidence for ferromagnetism in a

mixture of C_{60} and PTFCE subjected to heat treatment. In any report of ferromagnetism in an organic material, the purity of the starting materials is a critical issue and we have paid considerable attention to sample analysis. It is particularly important to make sure no magnetic impurities are present in the starting materials. The starting C_{60} was analyzed by induction coil plasma mass spectrometry (ICP-MS). The results indicated that signals from all metals were less than 1 part per billion (PPB). Electron paramagnetic resonance (EPR) of the C_{60} showed no evidence of the presence of magnetic elements or complexes. EPR is sensitive to 1 part in 10^{10}. A very narrow line at g=2.000 was detected which has previously been identified as the C_{60} anion.[13] The PTFCE was also subjected to detailed analysis. Energy dispersive x-ray spectroscopy of PTFCE showed only the presence of carbon, fluorine and chlorine, the constituents of the polymer. No other elements were detected. No magnetic species were detected by EPR. ICP-MS showed no magnetic metals above PPB in the PTFCE.

In a typical synthesis, 0.084 grams of PTFCE were dissolved in acetone and 0.040 grams of C_{60} added to the solution. The solution, while subjected to sonication, was allowed to slowly evaporate. The resulting residue was dried for some hours at 50 ^{0}C to remove any entrapped acetone. The composite was heated to 160 ^{0}C for two minutes and then rapidly quenched to room temperature

RESULTS

(a) PTFCE as a Source of Fluorine

PTFCE was heated to 160 ^{0}C for one hour and the Raman spectra recorded before and after the heating. No difference was observed between the frequencies of the Raman spectra indicating the material is not decomposing in the condensed phase.

However, the material sublimes at this temperature .In a second experiment the polymer was heated to 160 ^{o}C for one hour in a small beaker which was on a hot plate. The beaker had a chilled slide on the top which enabled collection of the condensed vapor. The Raman spectra of the material condensed on the slide is shown at the bottom of figure 1. On the top is the spectra in the same frequency region obtained from the polymer before heating. The two lines at 1198 cm^{-1} and 1298 cm^{-1},which are due to C-F vibrations, are completely gone in the spectra of the vapor indicating single fluorines are removed from the carbon atoms of the polymer in the vapor phase providing a source of atomic fluorine rather than diatomic fluorine.

(b) Magnetization Measurements

Figure 2 is a plot of the ac susceptibility versus dc magnetic field at 300 K for the heat treated C_{60}-TFPCE. The susceptibility has been normalized to the measured value at 3 Kilo Gauss. By comparing with a measurement on a sample of known magnetization, it is estimated the magnetization at 3000 Gauss is 0.07 emu/gm. No field dependent magnetization is observed in the separated starting materials subjected to the same treatment. Figure 3 shows the details at lower fields for increasing and decreasing dc magnetic field to and from 3000 Gauss showing a small hysteresis. Figure 4 presents the temperature dependence of the magnetization above room temperature measured in a 3000 Gauss field and normalized to its value at 300 K. A fit of this data to the Bloch equation,

$$M(T) = Ms(0)[\, 1 - AT^{3/2}] \qquad (1)$$

yields a value of A of 4.1246×10^{-5}. The temperature at which M(T) is zero, the Curie temperature, is estimated to be 837 K. from this fit This is likely an over estimate

because of deviations from the Bloch law near T_c due to critical fluctuations. However, it is close to estimates of the Curie temperature obtained in C_{60} photolyized in the presence of oxygen.

(c) Magnetic Force Microscope Measurement.

The PTFCE-C_{60} material which was heat treated was pressed flat on a slide in order to have a smooth surface. Figure 5 shows a magnetic force microscope image of the material. The brighter regions indicate areas of ferromagnetism.

(d) Ferromagnetic Resonance Measurements

The fluorine treated material was heated above its melting point and a 4000 G magnetic field applied. The material was then cooled below the melting temperature in the magnetic field. This aligns and locks in the direction of maximum magnetization parallel to the direction of the applied magnetic field. Figure 6 shows the ferromagnetic resonance spectra for the sample oriented perpendicular and parallel to the direction of the cooling field. For a particle having axial symmetry, the dependence of the field position of the FMR signal is given by,[14]

$$H_r = H_0 - H_A\,(1/2)(3\cos^2\theta - 1) \qquad (2)$$

where H_A =4 K/M is the anisotropy field , K is the magnitude of the anisotropy constant, and M is the magnetization. The angle, θ is between the direction of maximum magnetization and the applied dc field, H_r is the magnetic field at the center of the FMR signal and H_0 determines the g value. Because H_r is lower for the parallel orientation compared to the perpendicular orientation, it can be concluded that K is positive. Fitting the data in figure 6 to equation 2 allows determination of H_o and H_A. The values for H_o and H_A are 2730 G and 93 G respectively at 300 K. The g value is 2.287. One of the

characteristics of an FMR signal as opposed to an EPR signal is a strong temperature dependence of the line width and field position of the resonance. Figure 7 is a plot of the temperature dependence of the field position for the sample oriented perpendicular to the direction of the cooling field showing a pronounced decrease in the field position with decreasing temperature. Figure 8 plots the line width as a function of decreasing temperature showing a marked broadening as the temperature is lowered. The data in figure 7 and 8 confirm that the signal is an FMR signal.

(e) A Possible Model for the Origin of Ferromagnetism.

There has been a previous report of ferromagnetism in C_{60} subjected to a different fluorine treatment than used here.[15] It was observed in C_{60} ultrasonically dispersed in dimethylformamide (DMF) solution of polyvinyl difluoride (PVDF), $[H_2C\text{-}CF_2]_n$. However, the observed magnetism was not stable having a half life of 30 hours at room temperature. Further the results were only reproducible 1 out of 15 times. In our observation the results are stable over years and reproducible once the correct synthesis conditions are determined. However, an interesting observation in the PVDF solution made material is that ionization time of flight mass spectrometry showed the formation of C_{60} oligomers having fluorine atoms bonded to each C_{60} .

Previous Density Functional Molecular orbital calculations of the minimum energy structure of the F-C_{60}-C_{60}-F dimer indicated that the triplet state has a lower energy than the singlet state by 0.55eV.[16,17] This suggests that the fluorinated dimer could be a possible source of the unpaired spin necessary to form a ferromagnetic state. However a calculation of the bond dissociation energy (BDE) to dissociate the dimer into 2(F-C_{60})

indicate the dimer would not be stable above 400K in disagreement with experimental observations

As discussed in the introduction there have been a number of reports of ferromagnetism at lower temperatures in C_{60} subjected to heat treatment in the presence of I, IBr and H.[8-11] X-ray diffraction measurements of these materials indicated the ferromagnetism was arising from a cubic phase of C_{60} where the C_{60} was functionalized with halogens or hydrogens. This is a likely possibility for the structure of the ferromagnetic phase of the fluorinated C_{60} observed here. A calculation of the BDE to remove F from C_{60} gives a value of 4.36 eV indicating that C_{60}–F is stable above 400 K further supporting this possibility. [17]

There has been considerable work done on the fluorination of C_{60} which has been discussed in a number of reviews.[18,19] Generally the fluorination is achieved by exposing C_{60} to F_2 gas at high temperature .which of course results in $C_{60}F_N$ where N is even. An even N would have no net spin. The method of synthesis used here is likely exposing C_{60} to atomic fluorine produced by removal of F from the TFPCE polymer. This would result in N being odd giving the entity a net unpaired spin.

CONCLUSION

Field dependent ac susceptibility, ferromagnetic resonance and magnetic force microscopy clearly show that exposing C_{60} to fluorine at high temperature produces a ferromagnetic phase having a Curie temperature well above room temperature. The results can not be explained by the presence of magnetic impurities such as Fe, Ni or Co or compounds of them because ICP-MS and EPR of the starting materials indicate that such materials are present at less than one part per billion. While the structure of

the ferromagnetic phase is not determined some possibilities can be considered. Dimers of C_{60} have been suggested to be the origin of the unpaired spin. DFT calculations of the BDE of F-C_{60}= C_{60}–F indicate it unlikely to be stable above 400 K. On the other hand C_{60}–F is predicted to be stable at this temperature . This suggests the structure of the ferromagnetic phase may be cubic lattice of C_{60}–F , as observed for ferromagnetism in C_{60}–I, C_{60}–IBr, and C_{60}–H. However further work is needed to confirm this possibility.

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FIGURE CAPTIONS

1. Raman spectra before decomposition of PTFCE showing the C-F vibrations at 1198 cm^{-1} and 1298 cm^{-1} and decomposed vapor of PTFCE condensed on a cold slide (bottom) after heating to 160 ^{0}C showing absence of C-F vibrations.

2. Magnetic field dependence of the AC susceptibility measured at 300 K and normalized to its value at 3000 Gauss.

3. Magnetic field dependence of AC susceptibility at low fields for increasing and decreasing magnetic field to and from 3000 Gauss.

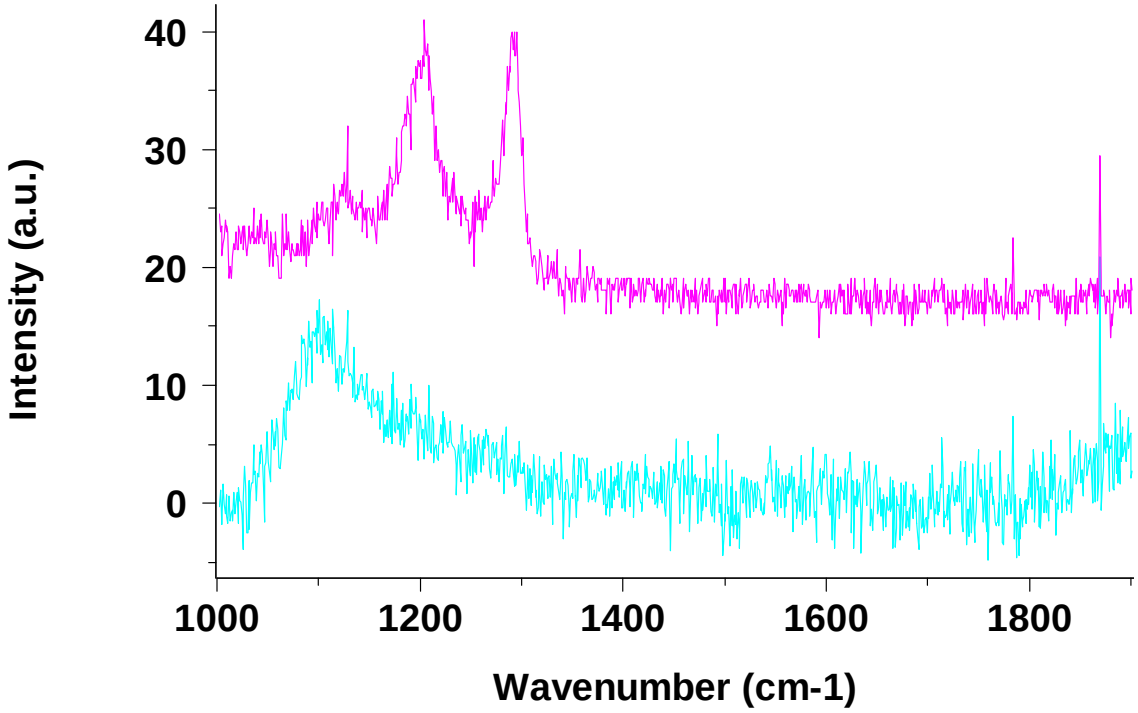
4. Temperature dependence of the magnetization above room temperature measured in a 3000 Gauss magnetic field and normalized to its value at 300 K.

5. Magnetic Force microscope image of the flattened surface of the heated treated polymer containing C_{60}. The units on the x and y axis are microns.

6. Ferromagnetic resonance spectra of the material melted and field cooled, as described in text, for the magnetic field parallel and perpendicular to the cooling field.

7. Temperature dependence of the field position of the FMR signal for the magnetic field perpendicular to the direction of the cooling field.

8. Temperature dependence of the line width of the FMR signal for the same orientation as in figure 7.


Intensity (a.u.)
40
30
20
10
0
1000
1200
1400
1600
1800
Wavenumber (cm-1)

.

Fig. 1

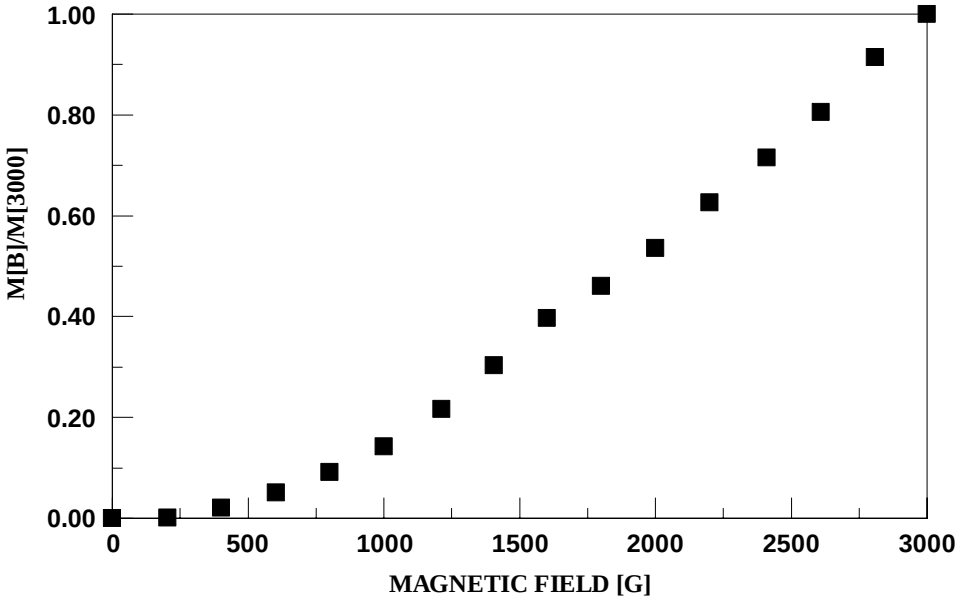

M[B]/M[3000]
1.00
0.80
0.60
0.40
0.20
0.00
0
500
1000
1500
2000
2500
3000
MAGNETIC FIELD [G]

Fig. 2

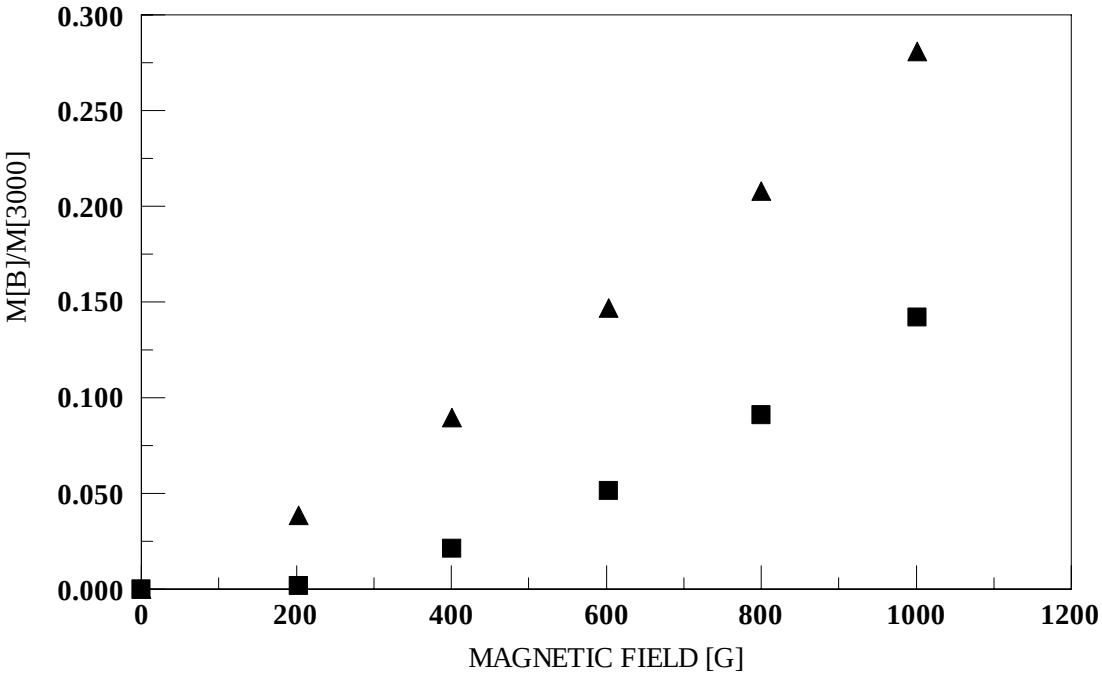

0.300
0.250
0.200
0.150
0.100
0.050
0.000
M[B]/M[3000]
0
200
400
600
800
1000
1200
MAGNETIC FIELD [G]

Fig. 3

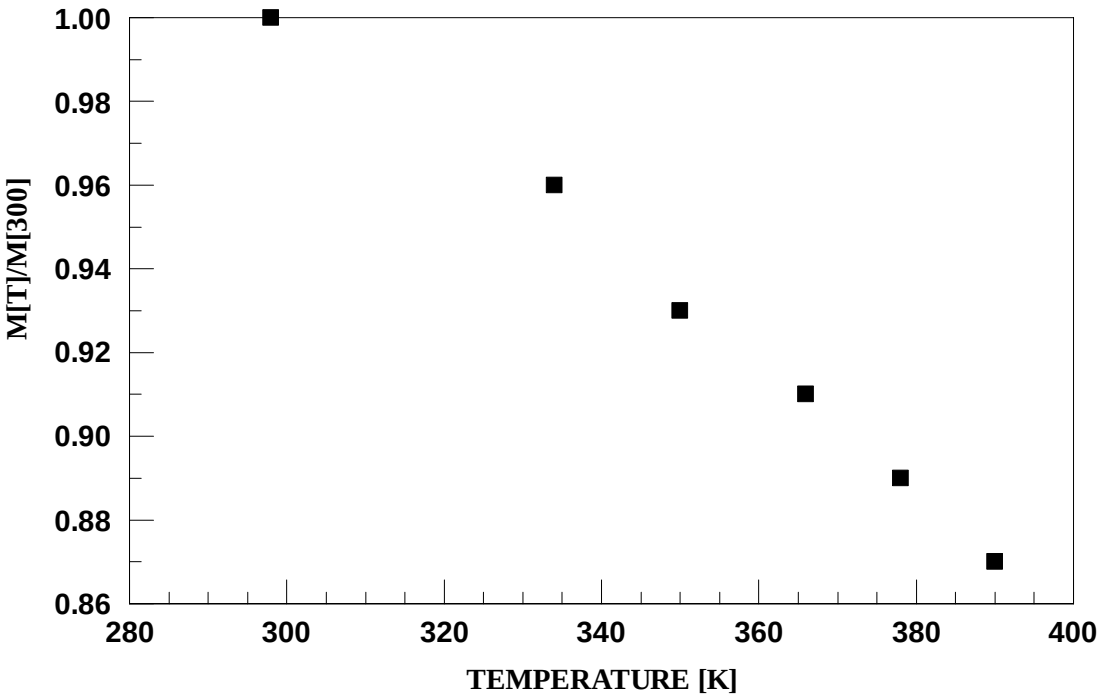

1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
M[T]/M[300]
280
300
320
340
360
380
400
TEMPERATURE [K]

Fig. 4

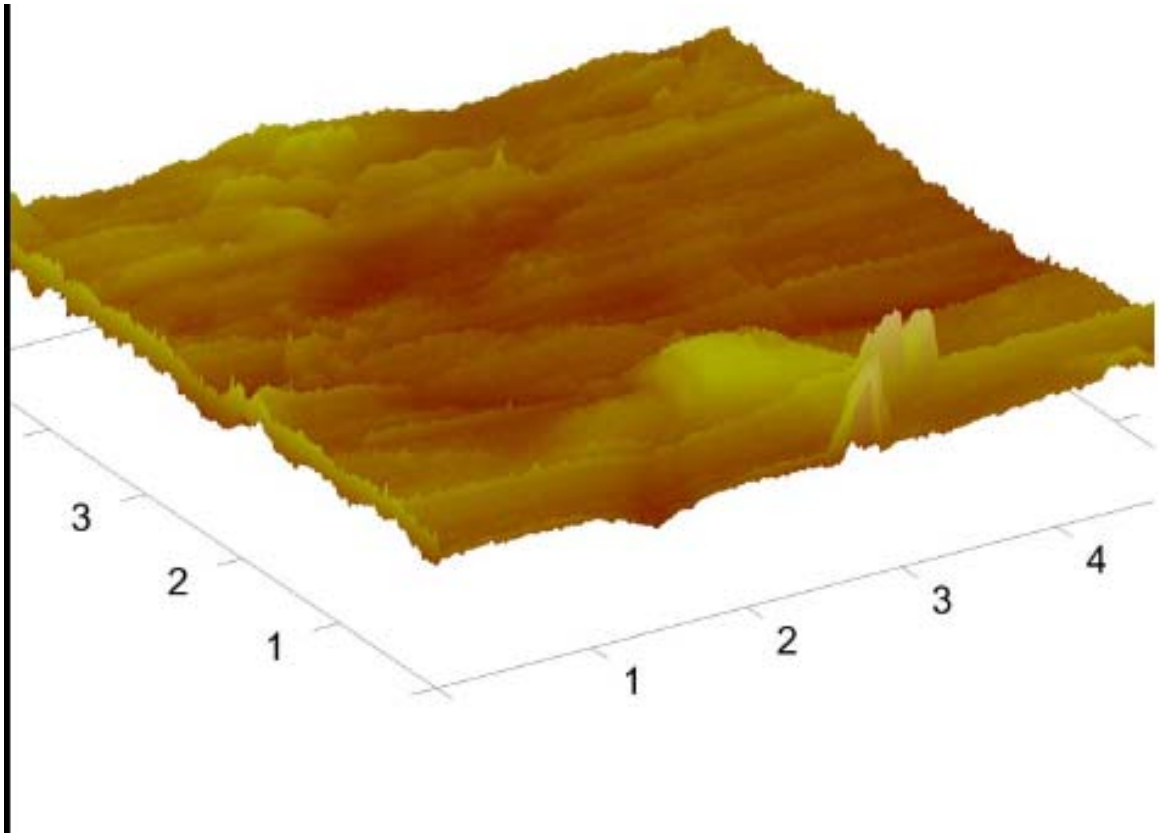


Fig. 5

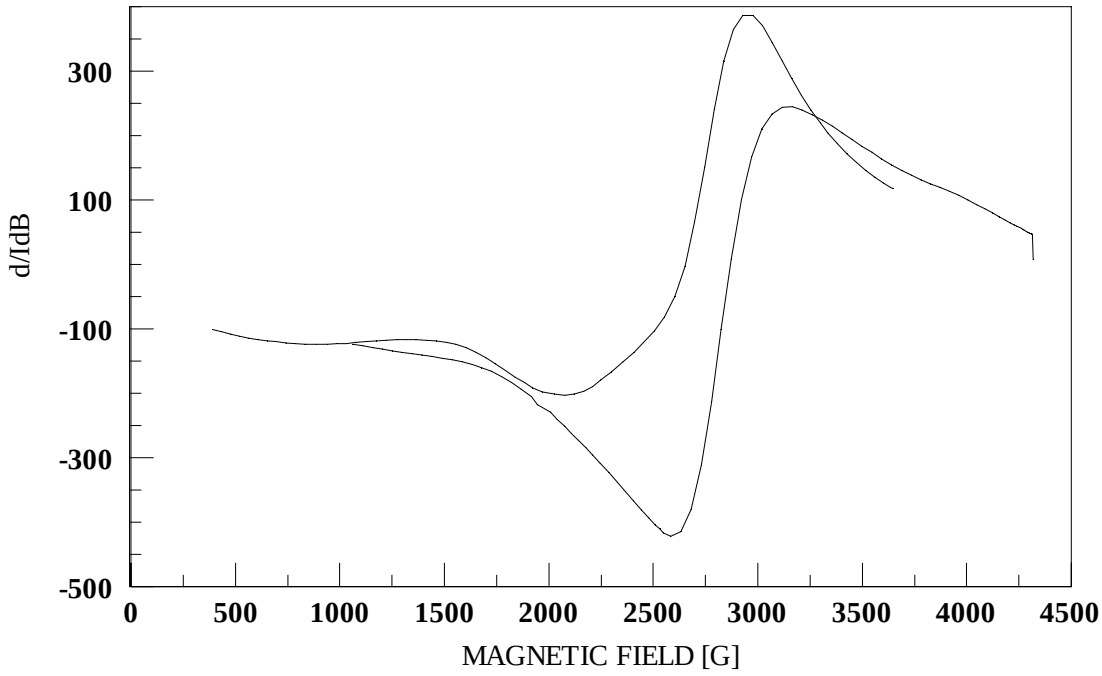

300
100
-100
-300
-500
d/IdB
0
500
1000
1500
2000
2500
3000
3500
4000
4500
MAGNETIC FIELD [G]

Fig. 6

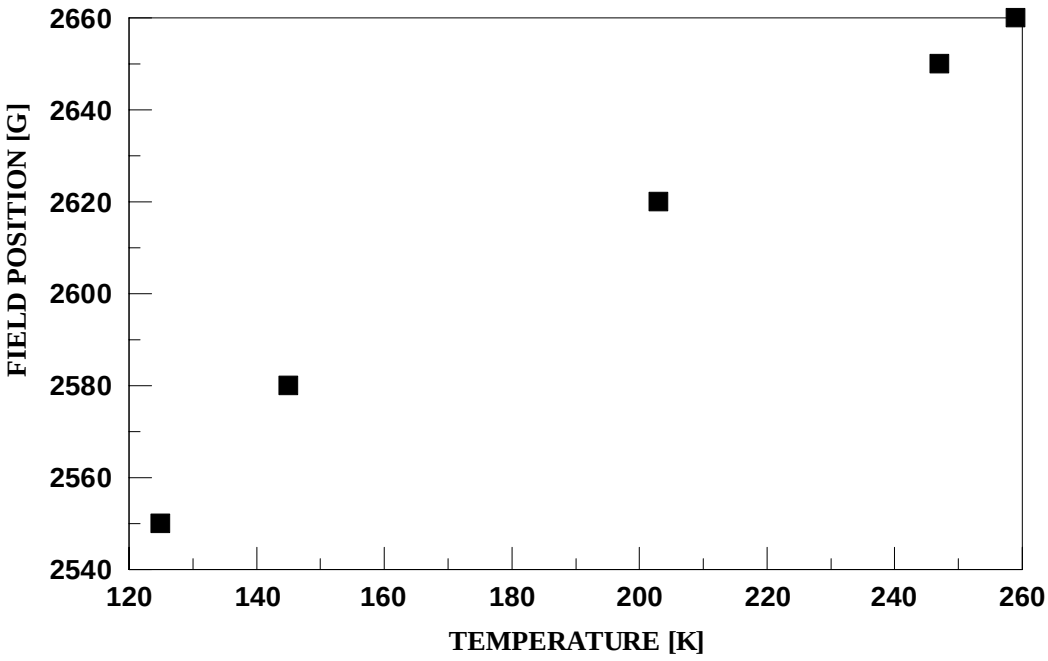

2660
2640
2620
2600
2580
2560
2540
FIELD POSITION [G]
120
140
160
180
200
220
240
260
TEMPERATURE [K]

Fig. 7

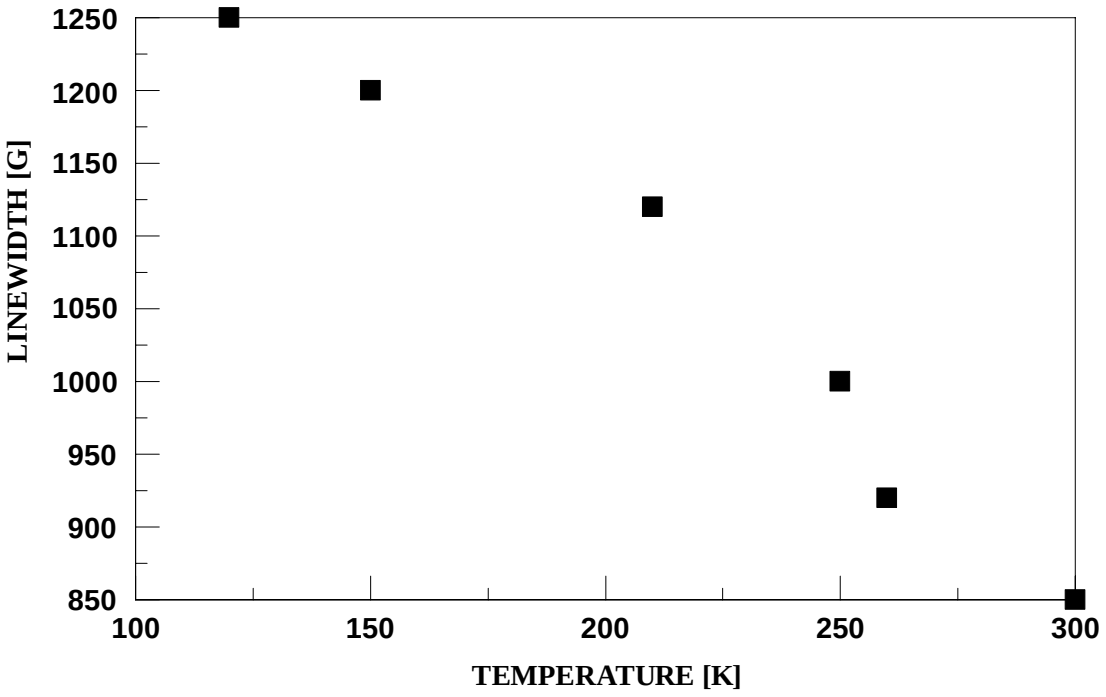

1250
1200
1150
1100
1050
1000
950
900
850
LINEWIDTH [G]
100
150
200
250
300
TEMPERATURE [K]

Fig. 8